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US-PAT-NO: 6508924

DOCUMENT-IDENTIFIER: US 6508924

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Control of breakdown products in electroplating baths

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Brief Summary Text -

BSTX (3):

made as required. However, other addition agents such as <u>brighteners</u>, leveling agents, suppressants, etc., together with impurities, cannot be individually analyzed on an economical or timely basis by a commercial platting shop. Their operating concentration is low and their quantitative analysis is complicated can be made regularly (such as pH measurement for acid con tent), and additions made as required. However, other addition agents such as $\frac{brighteners}{c}$ leveling Electroplating is a complex process involving multiple ingredient, in a plating bath. It is important that the concentration of several of the ingredients be kept with in close tolerances in order to obtain a high quality deposit. In some cases, chemical analysis of individual solution constituents and subject to error.

Brief Summary Text - BSTX (6):

metal where high quality plating is required. It is known that concentration of the organic additives, such as brighteners and within the plating solution The electroplating of through-hole interconnections in the manufacture multilayer printed circuit boards is an example of the use of an electropl metal where high quality plating is required. It is known that the during manufacture and use and to assure the proper the through-holes and leveling. The concentration of agents fluctuates because of oxidation the anode. recently. methods used to maintain a control concentration of the additive until brittleness and non-uniform deposition. Hull cell tests, Bone Pattern tests, and Pencil tests, combined with periodic additions of fresh additives, were the acceptable deposits on printed circuit boards. less than 100 parts per million parts of solution--ppm) in order to obtain within the plating solution must be maintained in low concentration proper mechanical properties for resistance to thermal stresses ire burned and powdery in appearance whereas excessive addition agents consequence chemical degradation. When the additive level is insufficient, These methods were unreliable and circuit board nce of these unreliable methods. The concentration of the organic additive This must be done to maintain brighteners and levelers, Reduction at quality suffered as an electroplating encountered the cathode, deposits (typically induce e f

Brief Summary Text BSTX (8):

U.S. Pat. No. 5,223,118 (gonnenberg et al.) discloses a method determining the quantity of brighteners and levelers present in an electroplating bath for the plating of printed wiring board substratthis method, the determination of both brightener and leveler is acc ä one step board substrates. In leveler is accomplished for

Detailed Description Text -DETX (4):

not limited surfactants, Many organic anic additives are used in metal electroplating baths, such as, but to, leveling agents, brighteners, accelerators, suppressors, wetting agents and the like. Certain organic additives are known during the electroplating process to form breakdown products.

(12) United States Patent Gomez et al.

(10) Patent No.:

(45) Date of Patent:

US 6,508,924 B1 Jan. 21, 2003

CONTROL OF BREAKDOWN PRODUCTS IN ELECTROPLATING BATHS (Sn) AN

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Inventors: Luts A. Gomer, Patchoque, NY (U)
Rozalis Beica, Bayport, NY (US);
Dents Morrissey, Huntington, NY
(US); Eugens N. Step, Newton, M.
(US)

5,935,402 A • 6,113,771 A • 5,223,118 A 5,252,196 A 4,089,754 4,132,605 4,917,774

10/1993 8/1999 9/2000 6/1993

Fisher

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Fanti

205/296 205/296 205/101 205/123 205/123

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6,224,737 B1 •

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Bui et al.

Landau et al. Sonnenberg et al. Somenberg et al. Fench et al. Tremmel et al.

Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 140 days.

Appl. No.: 09/384,124

 \mathfrak{g} Filed: May 31, 2000

(§ (£ U.S. CI. Par. C1.7 205/81, 205/82, 205/99, 205/123, 205/786.5; 205/787 205/81, 82, 99, 205/123, 157, 786.5, 787

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204/10

11 Claims, 5 Drawing Sheets

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Field of Search

3 Assignee:

(21)

(88)

Shipley Company L.L.C., Mariborough, MA (US)

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띪 FOREIGN PATENT DOCUMENTS 199 11 447 AI

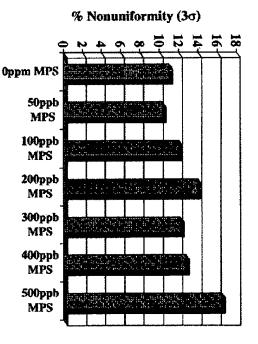
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cited by examiner

Assistant Examiner—William T. Leader (74) Attorney, Agent, or Firm—S. Mathew Cairus ઉ Primary Examiner—Nam Nguyen

ABSTRACT

products in electroplating baths as well as methods controlling the presence of such breakdown products Disclosed are methods for analyzing additive breakdown products F 8,



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PLATING APPARATUS

FOREIGN PATENT DOCUMENTS

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DOCUMENT-IDENTIFIER:

TITLE

Plating apparatus US 6379520 BI 6379520

U9-PAT-NO:

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Detailed Description Text -DETX (7):

copper electrode). The metallic ions emitted from the anode 1-3 are deposited on the surface of the substrate 1-4 to form a metal plating film. After continuously performing the plating process and processing a plurality of substrate 1-4, the composition, concentration, and amount of the plating solution 1-1 varies. In response to these variations, additive solution 2-4 from the replanishing tank 2-2 and plating solution 2-5 from the replanishing tank 2-1 to maintain the composition are concentration of the plating solution 1-1 at predetermined values. The additive solution 2-4 in the replanishing tank 2-2 is an organic additive With this construction, the power source 1-5 applies a predetermined voltage between the substrate 1-4 and anode 1-3, forcing metallic ions, such as Cu. sup.2+ to be emitted from the soluble anode 1-3 (for example, a phosphorous copper electrode). The metallic ions emitted from the anode 1-3 are deposited solution comprising a mixture of a polymer, leveler, carrier, and HCl.

Detailed Description Text - DETX (48):

tank 12-3, respectively, in order to maintain the composition and concentration of the plating solution 11-1 at predetermined values. The additive solution 12-7 contained in the replenishing tank 12-2 is an organic additive solution emount of the plating solution 11-1, fluctuates. Based on the state of these fluctuations, the regulating tank 12-1 is replenished with additive solution 12-7 or plating solution 12-8 from the replenishing tank 12-2 or replenishing With the construction described above, the power supply 11-5 applies a predetermined voltage across the substrate 11-4 and the anode 11-3, causing metallic ions such as Cu.sup.2+ to emit from the soluble anode 11-3 (which comprising a mixture of polymers, and after performing the process on a plurality of substrate S11-4, the composition and concentration of the plating solution 11-1, as well as the phosphorous copper electrode, for example) and deposit on the surface of the substrate 11-4 to form a metallic film. After continuous plating operations levelers, carriers, After continuous plating operations and HCL.

Claims Text - CLTX (13):
6. A plating apparatus according to claim 5, wherein said organic additive solution comprises a mixture of a polymer, a <u>leveler</u>, a carrier, and HCI.

Claims Text - CLTX (81): 42. A plating appara ndditive A plating apparatus according to claim 41, wherein said organic ve solution comprises a mixture of a polymer, a leveler, a carrie leveler, a carrier, and

Current US Original Classification - CCOR (1): $\frac{205/81}{}$

(12) United States Patent Kuriyama et al.

30 mm

(10) Patent No.: A STATE OF STREET

(45) Date of Patent: US 6,379,520 B1 Apr. 30, 2002

Inventors: Fumio Kurlyama; Hiroyuki Ueyama; Junitsu Yamakawa; Kenichi Suzuki; Atuzhi Chono, ali of Tokyo (JP)

ㅎㅎ cited by examiner 10-121297

Primary Examiner—Donald R. Valentine

Ebara Corporation, Tokyo (JP)

Notice: Subject to any disclaimet, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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 \mathfrak{E} Appl. No. 09/601,084

 \mathfrak{g} PCT Filed: Nov. 26, 1999

§ 102(e) Date: Jul. 27, 2000 § 371 Date: Jul. 27, 2000 PCT/JP99/06600

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PCT No.:

8 PCT Pub. No.: WO00/32850

PCT Pub. Date: Jun. 8, 2000

පි Foreign Application Priority Data

(51) Int. Cl.? . (52) U.S. Cl. . Nov. 30, 1998 Dec. 2, 1998 33 205/81; 204/238; 204/263 C25D 21/12 . 10-340576

(58) Field of Search 204/237, 2 204/232, 263, 269, 238; 205/82,

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3,658,470 A + 4/1972 Zievers et al. U.S. PATENT DOCUMENTS

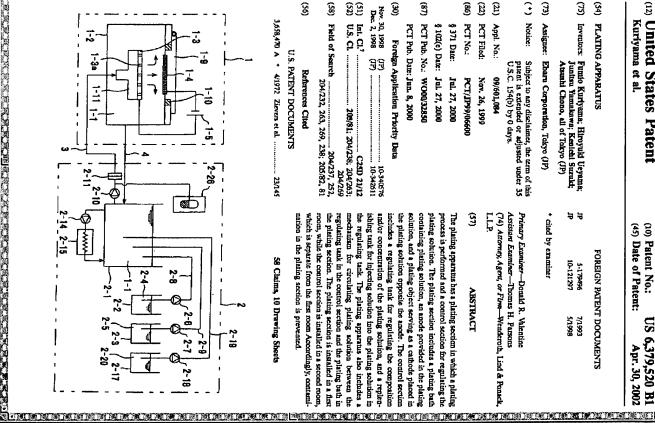
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(74) Attorney, Agent, or First—Wenderoth, Lind & Ponack, Assistant Examiner—Thomas H. Parsons

the regulating tank. The plating apparatus also includes a the plating solution opposite the anode. The control section nation in the plating section is prevented. which is separate from the first room Accordingly, contamiroom, while the control section is installed in a second room the plating section. The plating section is installed in a first regulating tank in the control section and the plating bath in mechanism shing tank for injecting solution into the plating solution in and/or concentration of the plating solution, and a replenincludes a regulating tank for regulating the composition solution, and a plating object serving as a cathode placed in containing plating solution, an anode provided in the plating plating solution. The plating section includes a plating bath process is performed and a control section for regulating the The plating apparatus has a plating section in which a plating for circulating plating solution between É

58 Claims, 10 Drawing Sheets

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TITLE: DOCUMENT-IDENTIFIER: US-PAT-NO: US 6458262 Electroplating chemistry on-line monitoring and control 6458262 BI

7 Jus 5906725 A

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Brief Summary Text - BSTX (6):

High-pressure liquid chromatography (HPIC) has been proposed as a method to monitor plating bath constituents by Taylor et al. "Electroplating Bath Control for Copper Interconnects," Solid State Technology, vol. 4, issue Nov. 11, 1998. In this article, the authors describe using HPIC to separate electrolyte species. Although HPIC techniques have improved dramatically over the post decade, this type of analysis has limitations with regard to plating bath composition. While organic additives such as accelerators, suppressors, and levelets are well suited for chromatographic separation, some important primary bath species, ions, metal salts, and acids are not. Analysis of purified bath components via chromatography can provide valuable information about organic components via chromatography can provide valuable information about organic plating bath electrolyte components, plating environment. but only provides a partial

Current U9 Original Classification - CCOR (1): $\frac{205/82}{}$

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 \mathfrak{g} Assignee: Novellus Systems, (US) Inc., San Jose, ς

Brain, Peter, "New Development in the Use of Cyclic Voltammetric Stripping for Analysis of Plating Solutions", pp. N1-N28. (Date of Publication Not Available).

Providence, Rhode Island, pp. 1-19. Date of Publication Not "Real Time Analyzer (RTA) Technical Manual", Technic, "Quali-Line" AC-1000", ECI Technology, 1993, pp. 1-2.

Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by \$3 days.

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(21) Appl. No.: 09/802,490

 \mathfrak{g} Mar. 9, 2001

(52) (2) Int. Cl.7 U.S. Cl. 205/82; 204/228.6; 204/229.2; 204/232; 204/237; 205/101 C25D 21/14

(58)

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Taylor, et al. "Electroplating bath control for copper inter-connectes", Solid State Technology, Nov. 1998, pp. 47-57. Whilel, et al., "Op-Line Monitoring of Gemical Processes in Electronic Components Manufacturing", Technic, Inc., pp. 1-8. Date of Publication Not Available. OTHER PUBLICATIONS

Primary Examiner-Nam Nguyen

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Assistant Examiner—William T. Leader (74) Attorney, Agent, or Firm—Beyet Weaver & Thomas, LLP

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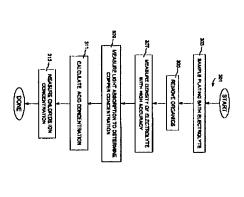
ABSTRACT

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The present invention provides methods and apparatus for analysis and monitoring of electrolyte bath composition. Based on analysis results, the invention controls electrolyte bath composition and plating hardware. Thus, the invention provides control of electroplating processes based on plating bath composition data. The invention accomplishes this by volyte is treated and analyzed in a flow-through system in order to identify plating bath component concentrations and based on the results, the plating bath formulation and plating process are controlled. incorporating accurate bath component analysis data into a feedback control mechanism for electroplating. Bath elec-

36 Claims, 5 Drawing Sheets

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US-PAT-NO: 5223118

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DOCUMENT-IDENTIFIER: US 5223118 A

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TITLE:

Method for analyzing organic additives in an electroplating bath

B B B B

Abstract Text - ABTX (1):

A direct method of analyzing <u>brighteners and levelers</u> used in metal electroplating baths. The method is based on the differential adsorption of these additives on a working electrode during a sequence of steps prior to and during metal plating. The sensitivity of the method allows for the determination of both <u>brightener and leveler</u> in the same sample without cyclic processing.

Brief Summary Text - BSTX (5):

ingredients be kept within close tolerances in order to obtain a high quality deposit. In some cases, chemical analysis of individual solution constituents can be made regularly (such as pH measurement for acid content), and additions made as required. However, other addition agents such as brighteners, leveling agents, suppressants, etc., together with impurities, cannot be individually analyzed on an economical or timely hasis by a commercial plating shop. Their operating concentration is low and their quantitative analysis is complicated Electroplating is a complex process involving multiple ingredients in plating bath. It is important that the concentration of several of the subject to error. ä

Brief Summary Text - BSTX (8):

and Pencil tests, combined with periodic additions of fresh additives, were the methods used to maintain a control concentration of the additive until recently. These methods were unreliable and circuit board quality until a consequence of these unreliable mathematicans. The electroplating of through-hole interconnections in the manufacture of multilayer printed circuit boards is an example of the use of an electroplating acceptable deposits on printed circuit boards. This must be done to maintain proper mechanical properties for resistance to thermal stresses encountered during manufacture and use and to assure the proper thickness of the deposit in the through holes and leveling. The concentration of the organic additive agents fluctuates because of exidation at the anode, reduction at the cathode, and chemical degradation. When the additive level is insufficient, deposits metal where high quality plating is required. It is known that the concentration of the organic additives, such as brighteners and levelers, within the plating solution must be maintained in low concentration (typically less than 100 parts per million parts of solution - ppm) in order to obtain

Brief Summary Text - BSTX (9):

was disclosed A more recent method for evaluating the quality of an electroplating bath ${f s}$ disclosed in Tench U.S. Pat. No. 4,132,605 (hereafter the Tench patent patent).

Sonnenberg et al. **United States Patent**

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Date of Patent: Patent Number;

Jun. 29, 1993 5,223,118

4,324,621 4/1982 4,443,301 4/1984 4,631,116 12/1986 4,725,339 2/1988 4,897,165 1/1990 4,917,774 4/1990

204/24 204/25 204/25 104/153 1

Assignee:	
Shipley Company Inc., Newton,	Sudbury, all of Maga.

OTHER PUBLICATIONS Fisher

[21] Appl. No.: 666,798

[73]

E	
File:	:
Mar. 8, 1991	

[88]	<u> </u>
427/10 [58] Field of Search	[51] List CL ³
Search	
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205/8	01N 27/
- 204/1	15/51/2 (7)
24.74 1.777	SD 21/1 04/153.1

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5	1/1979	12/1975	S. PATI
?	Teach e	Costas	ENT DO
121/151	T/102	3,925,168 12/1975 Costas 204/153.	U.S. PATENT DOCUMENTS

[34] METHOD FOR ANALYZING ORGANIC ADDITIVES IN AN ELECTROPLATING Wade Soanenberg, Foxborry, Roger Bernards, Wellesley, Fatrick Honle, Framinoham: Gardon Fither. Tench et al., Pulse Voltommetric Stripping Analysis of Acid Copper Flating Baths, J. Electrochem, Soc., Apr. 1985, pp. 831-834.

[75] Inventors:

Primary Examiner—John Niebling American Examiner—William T. Leader Attorney, Agent or Firm-Robert L. Goldberg **ABSTRACT**

A direct method of malyzing brighteners and levelers used in metal electroplating baths. The method is based on the differential alsorption of these additives on working electrode during a sequence of steps prior to and during metal plating. The sensitivity of the method allows for the determination of both brightener and leveler in the same sample without cyclic processing.

19 Claims, 9 Drawing Sheess

